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Synthesis and characterization of 3D modulated and smooth TiO_2 nanotubes for energy applications.

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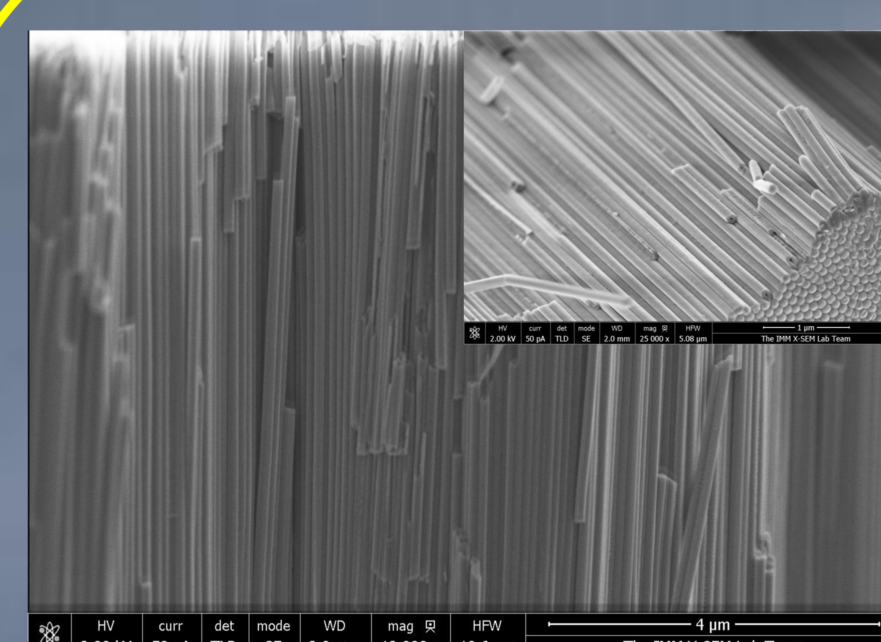
Introduction

- For more than a decade anodic TiO_2 nanotubes layers (TNTL) have attracted the attention of many research groups, with more than 5000 publications in the 2009-14 period.[1] This interest bases on their fast and easy synthesis processing and obviously to their optimal characteristics for different fields of applications ranging from biomaterials to water remediation and solar cells.
- The TNTL can be obtained by galvanostatic (GA) or potentiostatic (PA) anodization.[1]. Pulsed GA and PA can be employed to synthesize 3D Modulated TNTL (3D-TNTL). 3D TNTL present several advantages compared to smooth TNTL i.e. higher surface/volume ratio and photonic properties.[3]
- Annealed TNTL (anatase phase) have been employed in Dye Synthesized Solar Cells (DSCs) and more recently in Perovskites based solar cells n-type contact.[4] For these applications the Contact Potential Difference (CPD) between Metal/TNTL is of critical importance for device designing.
- In this work we have characterized and compared the CPD between Au/3D-TNTL and Au/smooth TNTL

Experimental

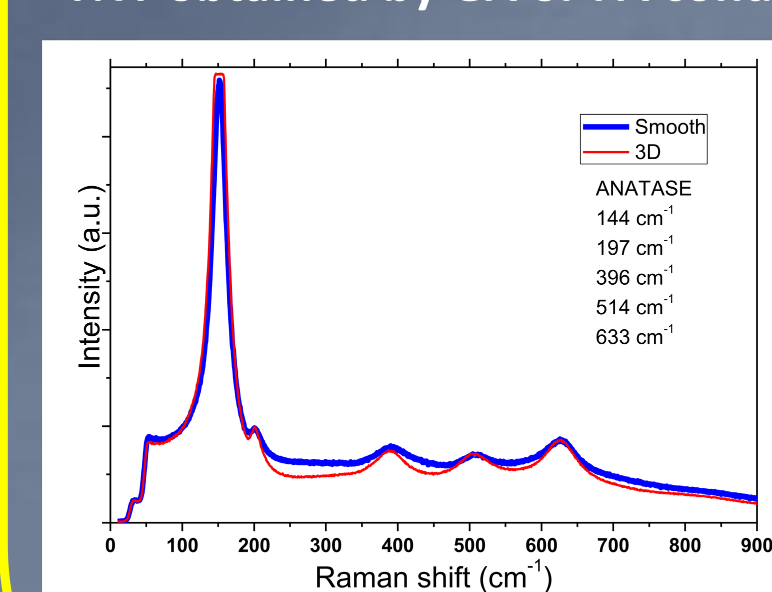
i) TNTL layers were obtained by anodization of Ti foils (97%) in a Ethylene Glycol, NH4F (0.5 wt%) and DI water (2%) composed electrolyte. For smooth TNTL the anodizations were carried out at constant voltage (50 V) and constant current (j=7.8 mA cm^{-2}). For 3D TNTL pulsed anodization conditions were applied:
-PA: 40 x (V=50 V(25'')+ V=10 V (60''))
-GA: 40 x (j=7.8 mA cm^{-2} (25'')+ j=0 (60'')).
ii) TNTL were annealed in a RTA furnace at 450 ºC (1 ºC s^{-1}) for 1 hour in forming gas atmosphere.
iii) Raman Spectroscopy was carried out with a Jobin Yvon LabRam HR using a Nd:YAG laser of 532 nm wavelength.
iv) 50 nm thick Au contacts were deposited on TNTL by e-beam deposition (48.0 mA, 0.8 Å s^{-1} , $7\cdot10^{-7}$ mbar) through micrometric mask.
v) SEM characterization was performed with a FEI Verios 460 microscope.
v) AFM (NANOTEC) was employed to perform Kelvin Probe Microscopy. The perturbation in the measure is attributed at the conducting samples, however the KPM technique is minimizing the electrostatic interaction due to changes on surface potential using a Cr/Pt conductive coating tip (EFM mode, force modulation, resonant frequency 75 KHz and force constant 3 N/m. Images were acquired at scan rates of 0.01 Hz, Bias DC potential of maximum 7 Volts and Bias AC frequency 7000 Hz.

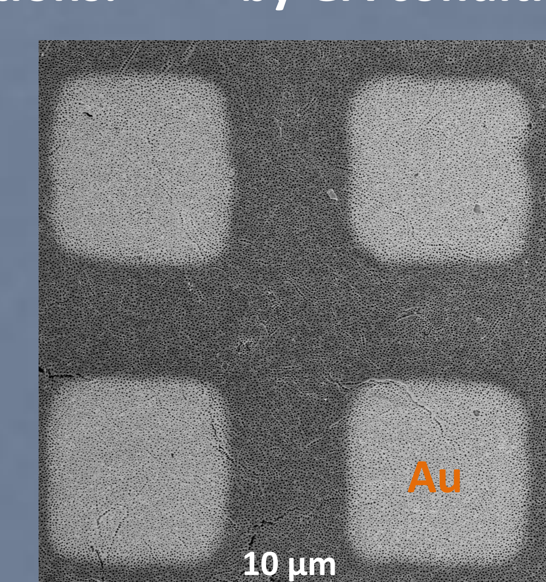
Results: Morphology and structure

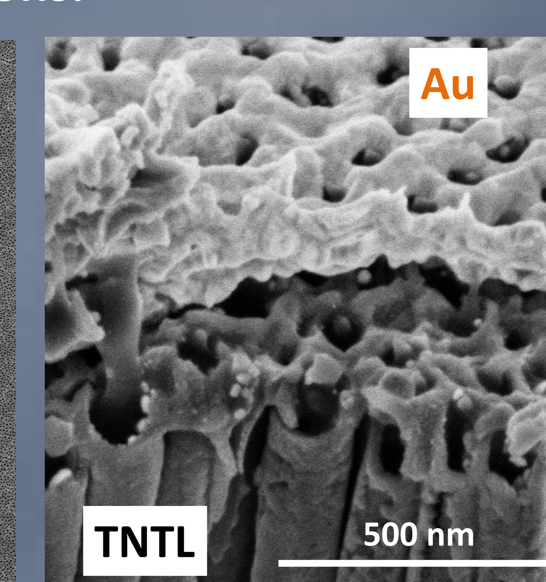


No evident differences between smooth TNT obtained by GA or PA conditions.

Better modulation of 3D TNTL obtained by GA conditions.

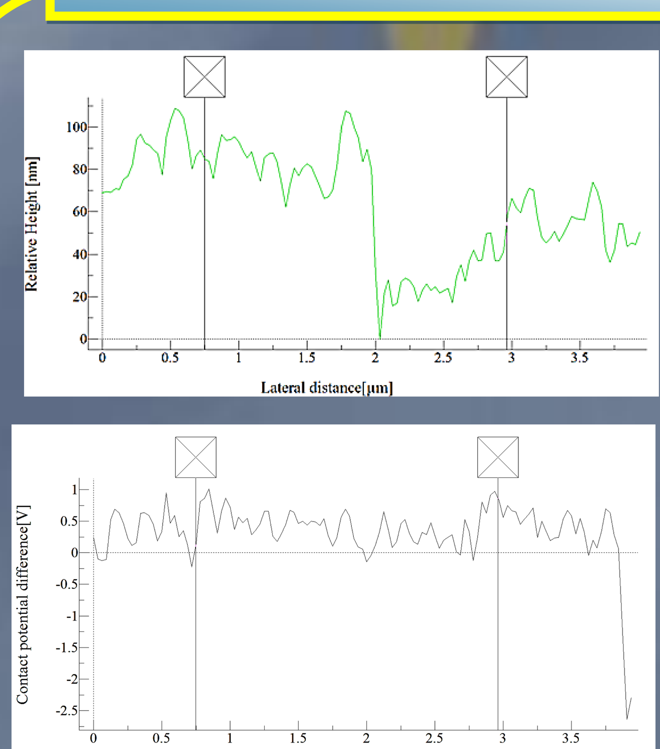


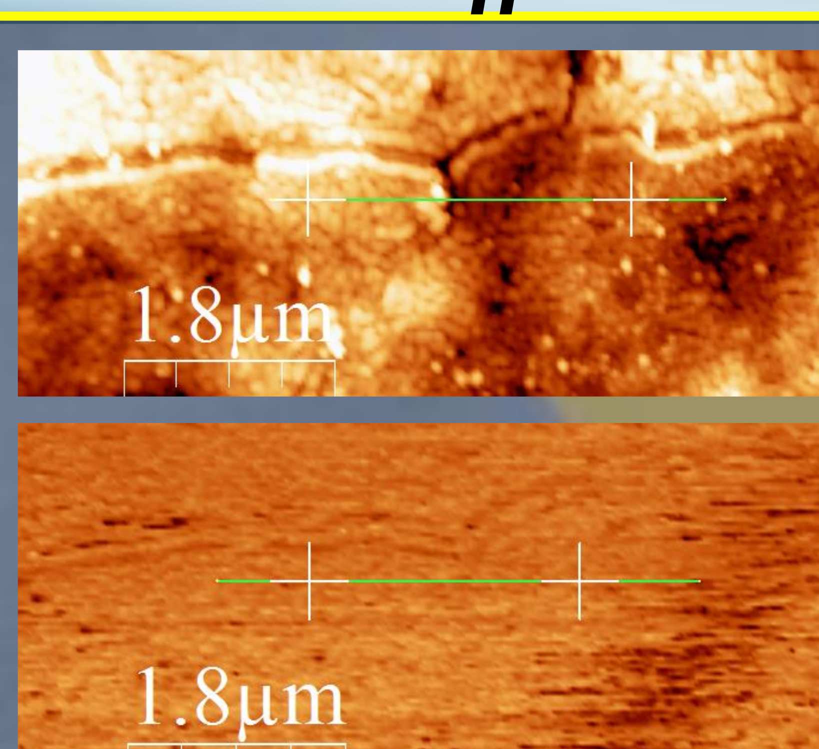




No evident structural or compositional differences between annealed smooth and 3D TNTL. Well defined and conformal growth of Au on smooth and 3D TNTL.

Results: Contact Potential Difference





All the scanned surfaces (smooth and 3D TNTL) presented a homogeneous voltage profile in the Au and TNTL regions, around 0.5 V of CPD respect to the tip. The obtained results are within the experimental error of previous works.[5]

Conclusions

- Smooth and 3D modulated TNTL have been synthesized under GA and PA conditions, and characterized.
- No evident changes structure and composition between both types of nanostructures.
- Similar CPDs were obtained for smooth and 3D modulated TNTL under applied measurement conditions.
- These results suggest that the 3D modulation of TNTL should provide increased surface/volume ratio without noticeable changes regarding structure, composition or work functions.

References

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